ON ANOMALOUS DEPOLARIZATION OF THE LIGHT SCATTERED BY BINARY MIXTURES

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PART I

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ABSTRACT The distribution of intensity in the "wing" of the Rayleigh line due to a binary mixture of CS_2 and CH_3OH at the critical solution temperature as well as the dependence of the value of ρ_h of the light scattered by a similar mixture of phenol and water on the shape of the illuminated volume have been experimentally investigated. The results do not seem to support the theory of formation of "clusters" put forward by Krishnan.

1. INTRODUCTION

Krishnan[1] has recently observed that the light scattered along the direction of the incident electric vector by some binary mixtures at the critical solution temperature is polarized in a way not expected from the primitive theory of light scattering. Thus it is found that with the incident vibration in the horizontal direction, the ratio of intensity of the horizontal component to that of the vertical may be as much as 5, while from the primitive theory of molecular scattering of light, this should be unity. This anomaly has been explained by Krishnan by assuming that large clusters of molecules are present at and near the critical solution temperature, so that the fundamental assumption in the primitive theory that the size of the scattering particles is small compared to the wave-length of incident light cannot now be made. The theory of scattering by large particles had already been developed by Lord Rayleigh,[2] Mie,[3] and Shulejkin,[4] and Krishnan based his conclusions on the results of investigation of these authors. Later, Gans,[5] Vrkljan and Katalinic[6] have made theoretical investigations on the relation between values of factor of the depolarization and the shape and size of the scattering particles.

The same subject of light scattering along the direction of incident vibration in binary liquid mixtures has however been independently studied experimentally by Rousset,[7] who also observed the value of ρ greater than 1, and put forward the theory that the anomalous depolarization is due to secondary scattering. There is a fundamental difference between Rousset's explanation and that offered

by Krishnan. Rousset does not assume any definite size of the scattering particles but since he integrates the secondary scattering over the illuminated volume of the liquid, the value of ρ depends on the shape of this illuminated volume. In Krishnan's theory, on the other hand, the secondary scattering is not taken into consideration at all, and since only the primary scattering by large particles is considered the value of ρ should not depend on the shape of the illuminated volume. It is evident therefore that both the explanations cannot be simultaneously correct. It was, therefore, thought worth while to investigate experimentally how the intensity of the wing accompanying the Rayleigh line is affected by the formation of the so called " swarms " in opalescent mixtures and also whether the shape of the illuminated volume of the mixture actually affects the value of ρ, the factor of depolarization of the light scattered in the direction of the incident light vector, and the present investigation was therefore undertaken.

As mentioned before, the experimental study consists of two parts :

(A) In the first part is studied the wing of the Rayleigh line produced by a critical solution of three parts by weight of carbon disulphide and one part of methyl alcohol, with incident unpolarized light.

(B) In the second part is studied the depolarization of the light scattered along the direction of the incident vibration for a critical solution of 34% by weight of phenol in water and for different shapes of the illuminated volume of liquid.

(A) *Wing of the Rayleigh line*

Both the liquids CH_3OH and CS_2 were purified by distillation in double bulbs. The solution of CS_2 in CH_3OH was contained in a vertical glass tube, 2 cms. in diameter and occupied a length of 6 cms. of the tube. A part of this tube was immersed in a glass cell containing water and maintained at the critical solution temperature, *viz.*, about 41°C, by placing a covered electric lamp below. The light from a Hg arc was focussed on to the liquid by a large condenser and the light scattered in a perpendicular direction was spectroscopically analysed. A Fuess spectrograph having optical parts of glass and a dispersion of about 11·5 Å per mm. in the region of 4047 Å was employed. The spectrum was photographed on a Golden Isozenith plate and the microphotometric record was obtained by means of a Moll self-registering microphotometer. The true intensity curve was then obtained in the usual way from blackening—log intensity curves.

RESULTS

TABLE I.

Intensity Distribution in the Wing for the Critical Mixture CS_2 + CH_3OH

$\Delta\nu$ in cm.$^{-1}$	10·5	21·0	31·5	42·0	52·5	63·0	73·5	84·0
Int.	154·0	106·9	80·7	63·0	51·8	36·7	27·2	19·8

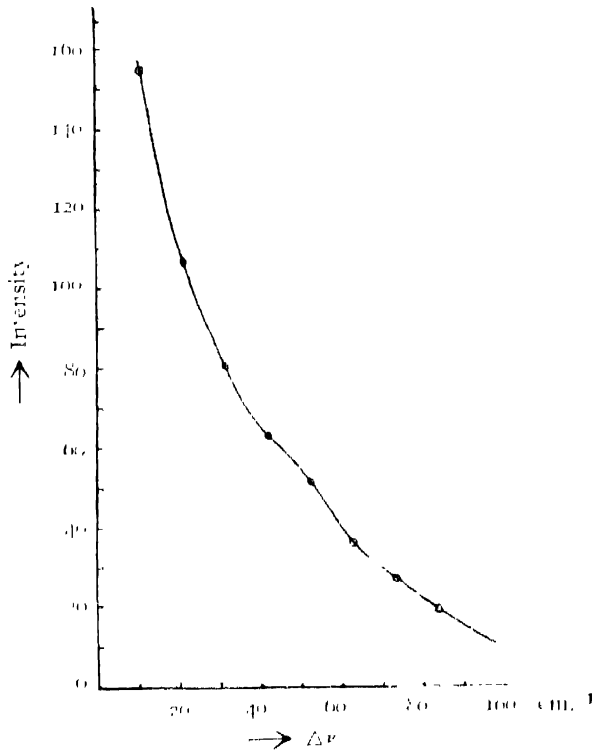

FIGURE 1.

The intensity distribution in the wing on the Stokes side is graphically represented in figure 1. It will be observed that there is an inflection in the curve at about 50 cm.$^{-1}$ from the centre of the Rayleigh line and the wing extends to about 120 cm.$^{-1}$ On comparing the plate for the opalescent solution with that due to a 30% solution of CS_2 in CH_3OH no noticeable change in the intensity of the wing relative to the Raman line at 655 cm.$^{-1}$ was observed.

(B) *Depolarization of Light Scattered in the Direction of Incident Light-Vector*

A 34% solution of Merck's crystallised phenol in distilled water was taken in a rectangular glass vessel which was kept immersed in water in a wide beaker. The beaker was electrically heated by means of some coils of resistance wire placed below and the temperature was maintained at about 65°C which was found to be the solution temperature. The light from a point-o-light lamp was made parallel by a convex lens and then a nicol was interposed in its path so that the incident electric vector was horizontal. The light scattered in a perpendicular direction in horizontal plane was observed through a combination of a Wollaston double image prism and a nicol. For separation of the two components by the Wollaston prism a rectangular slit (4 mm. × 2 mm.) was interposed in the path of the scattered light, and for better parallelism of the rays another slit of the same size was interposed just before the observation nicol. The ratio of the intensities in the horizontal and vertical components was obtained in the Cornu method by visual observation. If θ be the angle from the horizontal plane to the transmission plane (short diagonal) of the nicol when the two images are of equal intensity then

$$\frac{\text{Intensity of the horizontal component}}{\text{Intensity of the vertical component}} = \tan^2\theta.$$

The experiment was repeated with different shapes of the illuminated volume of the opalescent mixture.

RESULTS

In one case the illuminated portion of liquid had nearly the shape of a cube of sides 2·8 cms. placed so that two parallel faces were vertical and perpendicular to the incident beam and the other faces made an angle 45° with the vertical. In the other case the illumination volume was of the shape of a rectangular lamina so placed that the four narrow sides were all vertical and all the edges were either parallel or perpendicular to the incident beam. In this case, the sides of the rectangular lamina were 5 cm., 2·8 cm. and 0·4 cm. respectively. The ratio of the length to the thickness of the rectangular lamina was thus about 12. The mean of the several readings for the depolarization factor for the above two cases of the illuminated volume are given in table II.

TABLE II.

Values of ρ for two Different Shapes of Illuminated Volume with Critical Solution of Phenol + Water.

Shape of Illuminated Volume.	θ.	$\rho = \tan^2\theta$.
Cube	46°	1 (approx.)
Thin Rectangle	60°	3

DISCUSSION

The intensity distribution in the wings for pure CS_2 and for 30% mixture of CS_2 in CH_3OH at the ordinary temperature is given in another paper.[8] It will be found in all the cases that there is an inflection in the curve at about 50 cm.$^{-1}$ Further the extension of the wing in the critical solution is also the same as in the pure liquid and in the 30% solution. This shows that the rotation of the molecules which gives rise to the wing is not appreciably diminished in the critical solution. But, if, as postulated by Krishnan, the molecules form clusters of definite shape and size, such as thread-like, then it seems that the rotation of the molecules in these clusters should be much hindered. The absence of such hindrance cannot however conclusively invalidate Krishnan's theory, since even in clusters rotation about some axis may be possible.

On the other hand the observation on the depolarization for different shapes of the illuminated volume cannot at all be explained by Krishnan's theory. According to this theory the depolarization factor should be the same for all shapes of the volume illuminated, as it must, depending only on the shape and size of the molecular clusters. But in the actual experiments described above such divergent values as 1 for a cube and 3 for a rectangular lamina are obtained for the depolarization factor.

This is, however, quite in agreement with Rousset's theory. According to this theory the scattering in the direction of the incident vibration is due at the critical solution temperature, for the most part, to the rescattering of the light scattered from the liquid. At the critical solution temperature the isotropic scattering is very high in proportion to the anisotropic scattering and the depolarization factor for the natural incident light becomes almost zero, as shown by Rousset. Hence the light scattered in the direction of the incident vibration may be supposed as mostly due to the secondary scattering. When the temperature is raised, the secondary scattering diminishes and ultimaley the anisotropic scatering predominates. Hence though at temperatures sufficiently removed from that of

critical solution the depolarization in the direction of incident vibration should be perfect, the depolarization at and near the critical solution temperature may not be so.

For a clear understanding of the effect of secondary scattering, we shall go into Rousset's calculation in some detail. Let the incident light vibrate in the direction of the Y-axis which is also the direction of observation. Let the origin of co-ordinate be taken at the centre O of any volume element in the scattering medium and let the polar co-ordinates for the centre M of any other volume element dv be r, θ, ϕ. Consider light scattered from M to O. For this, resolve the light vector V of the primary scattering which vibrates parallel to OY (neglecting anisotropy) into one component, V_1, perpendicular to the meridian plane through M and another V_2, tangent to the meridian circle. These two components are respectively proportional to $\cos\phi$ and $\sin\phi\cos\theta$ and their resolved parts parallel to the z- and x-axes are given by

$$V_{1z} = -V\cos\phi\sin\phi \qquad V_{1x} = 0,$$

$$V_{2x} = V\sin\phi\cos\phi\cos^2\theta, \qquad V_{2z} = V\sin\phi\sin\theta\cos\theta$$

The above components are in phase and the square of the electric moment induced parallel to OX and OZ at O, are proportional to

$$\frac{[\sin\phi\cos\phi(\cos^2\theta-1)]^2}{r^2}dv \text{ and } \left(\frac{\sin\phi\sin\theta\cos\theta}{r^2}\right)^2 dv$$

where $$dv = r^2\sin\theta d\theta d\phi dr.$$

Thus the intensity of the secondary scattering along OY, resolved parallel to OX and OZ, are given by omitting a common factor in both,

$$X_y = \iiint_V \sin^5\theta\cos^2\phi\sin^2\phi d\theta d\phi dr$$

$$Z_y = \iiint_V \sin^3\theta\cos^2\theta\sin^2\phi d\theta d\phi dr$$

where the integral is to be taken over the illuminated volume V of the scattering medium and the suffix 'y' in the left denotes that the incident light vector is parallel to OY.

If the illuminated volume has the shape of a sphere we shall find from the above formulae that X_y and Z_y have the same values as required by the symmetry. A similar result must also follow when the illuminated volume has any other shape which on being rotated through 90° about the axis of y coincides exactly with its original configuration.

Let the illuminated volume have the shape of a circular disc coaxial with the Z-axis and with centre at O.

Let the radius of the disc be R and its height 2H. The expression for X_u and Z_u become easily integrable on transforming to cylindrical polar co-ordinates and it is found that

$$X_u = \frac{\pi}{4}\left(\frac{3}{4} R \tan^{-1}\frac{H}{R} - \frac{1}{4}\frac{R^2 H}{R^2+H^2} + H \log_e \frac{H^2+R^2}{H^2} \right),$$

$$Z_u = \frac{\pi}{4}\left(R \tan^{-1}\frac{H}{R} + \frac{R^2 H}{R^2+H^2} \right).$$

From these formulae it will be readily seen that in the secondary scattering the X and Z components are not of equal intensity. If, in particular, H is supposed small compared to R, then the above simplifies into

$$X_u = \frac{\pi H}{8}\left(1 - 4\log_e \frac{H}{R}\right),$$

$$Z_u = \frac{\pi H}{2},$$

and

$$\rho = \frac{X_u}{Z_u} = \frac{1}{4} + \log_e \frac{R}{H}$$

For $R = 10H$ the above gives $\rho = 2{\cdot}00$

In the actual experiments, however, of Rousset, as also in the present investigation, the illuminated volume was of the shape of a rectangular parallelopiped. If $2a$, $2b$, $2c$ be the lengths of the edges which are parallel to the co-ordinate axes along OX, OY, OZ respectively, then the values of X_u and Z_u, using cartesian co-ordinates, become

$$X_u = 8\int_0^a \int_0^b \int_0^c z^2 y^2 (x^2+y^2+z^2)^{-3}\, dx\, dy\, dz,$$

and

$$Z_u = 8\int_0^a \int_0^b \int_0^b x^2 y^2 (x^2+y^2+z^2)^{-3}\, dx\, dy\, dz.$$

Calculating for the case when $\frac{c}{a} = \frac{1}{10}$, Rousset finds that the depolarization factor is 3·0.

The two results of Rousset's theory, *viz.*, (*i*) that for an illuminated volume symmetrical about the y-axis the depolarization factor should be unity and (*ii*) that for the rectangular parallelopiped with the dimension, $\frac{c}{a} = \frac{1}{10}$, the depolarization factor should be about $\frac{1}{3}$, are well verified by the present investigation. It is to be pointed out, however, that though the volume in the first case, when $\rho = 1$ was not strictly symmetrical about the y-axis, the deviation from symmetry is not so serious as to materially affect the value of $\rho = 1$.

It thus appears that the anomalous depolarisation of the light scattered by binary mixture at the critical solution temperature may be a geometrical effect arising from secondary scattering rather than the effect of the formation of large clusters of molecules.

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Part II

Krishnan in a recent paper* has questioned the validity of the explanation put forward by A. Rousset (Theses, Paris, 1935) to account for the anomalous depolarization of the light scattered by binary mixtures at the critical solution temperature. The evidences cited by Krishnan seem not to be conclusive, for reasons stated below.

The first evidence advanced by Krishnan against Rousset's theory is that the depolarization factor ρ with incident unpolarized light for a critical water-isobutyric acid mixture should be, on Rousset's theory, ρ_u | = ·003%, while experi-

*The *first part* of this paper was written in April, 1937 but could not be published earlier as it formed a part of the *thesis* for the degree of M.Sc. The *second part* was written on seeing the paper by R. S. Krishnan (Proc. Ind. Ac. Sci., A., 5, 577, 1937).

†In this Part we adopt for the deplorization factor the notation used by Krishnan.

mentally this is 1·5%. Such a statement is, however, not correct. Because, firstly, the value ·003% is a miscalculation. the value calculated on Rousset's theory with the data assumed by Krishnan is not ·003% but ·025%. Secondly, the data assumed by Krishnan are again not the correct ones. It will be found on p. 77 of Rousset's *Theses* that the experimental value 1·5% is for the temperature $\Delta T = T - T_{crit} = 0{\cdot}15°C$ and not for the temperature $\Delta T = 1°C$ as stated by Krishnan and to which the above calculation, ·025%, applies. On p. 128 of Rousset's *Theses* are given the data for the Rayleigh constants with white and blue light for the water isobutyric acid mixture for the temperature $\Delta T = 0{\cdot}4°C$. We can take the same values for the temperature $\Delta T = 0{\cdot}15°C$ without sensible error, and in any case the Rayleigh constant for $\Delta T = 0{\cdot}15°C$ should never be smaller than that for $\Delta T = 0{\cdot}4°C$.

Now $$\rho_u = \frac{\text{Horizontal component}}{\text{Vertical component}}.$$

Disregarding for the present the orientation scattering we can suppose the primary scattering as completely polarized. Then it follows that the horizontal component is due solely to the secondary scattering while in the vertical component the secondary scattering is negligible compared to the primary scattering. Then we have, remembering that the primary scattering is bluish,

$$\rho_u \backsim \frac{R_{white} \times R_{blue}}{R_{white}}$$

$$= 0{\cdot}9\% \text{ (from Rousset's data)}$$

while the experimental value is 1·5%. The effect of the orientation scattering will be to slightly increase the value 0·9%.

The second evidence cited by Krishnan is that if, after Rousset's theory, the econdary scattering is calculated by the formula

$$\rho_h = \frac{O}{O+S}$$

where ρ_u = depolarization factor with incident horizontal vibration,
O = orientation scattering,
S = secondary scattering,

then the secondary scattering is not found to vary at the same rate as the primary scattering (R) which it ought to have according to Krishnan. Both the above formula and the argument are however, incorrect. We should instead have, firstly,

$$\rho_h = \frac{O+\chi S}{O+S}$$

where χ is the depolarization factor of the secondary scattering alone. Secondly, it is not true that S should vary as R, but indeed as R^2 in the absence of any

absorption in the medium while actually there being greater and greater absorption as the critical solution temperature is approached the actual variation follows a more complicated law.

Two other objections raised by Krishnan relate to the dissymmetry of scattering and the λ^{-4} law. These points have been discussed in detail by Rousset and satisfactorily explained without any recourse to the postulate of "Schwarmbildung."

The theoretical variation of ρ_u with dimensions of the illuminated volume, on Rousset's theory, is mentioned by Krishnan, but not discussed thereafter. His values as given in table III of the paper, however, shows that ρ_h is the same for two different shapes of the vessel, while according to Rousset's theory such should not have been the case. In our experiment, on the contrary, as mentioned in the first part, *we found a definite variation of* ρ_h from 33% to 100% as the volume was changed from a rectangular lamina to a cube.

The dispersion of depolarization, as found from table III of Krishnan's paper, is, however, in good agreement with Rousset's theory. For the depolarization factors ρ_u, ρ_l being proportional to R it follows that these values for the blue light should be $\frac{\lambda^{-4}_{\text{blue}}}{\lambda^{-4}_{\text{orange}}}$ times that for orange light.

The variation of ρ_u, ρ_v, ρ_h in the background scattering with distance from the centre of the track of light in the medium is found for a critical phenol-hexane mixture and also for an opalescent caesin solution, and it is thereby concluded by Krishnan, that the two cases are similar. The table given by Krishnan, however, scarcely allow such a conclusion to be drawn. Thus ρ_h for the phenol-hexane mixture increases from 36% to only 40% when the slit is taken from the centre to the periphery of the track while for the case in solution the value increases from 42% to almost the full value 95%. For the same movement of the slit ρ_u for the critical solution increases 9 times while that for the caesin solution increases 13 times and ρ_v for the critical solution increases 9 times while that for the case in solution, 15 times.

Thus the evidences cited by Krishnan do not allow any conclusion to be drawn as to the reality of the molecular clusters, while *the definite proof as to the existence of a considerable secondary scattering clearly shown in the appreciably illuminated background* and the satisfactory explanation of all the optical anomalies by its means constitute a strong argument in favour of the point of view expressed in the first part of this paper.

In conclusion I wish to express my grateful thanks to Prof D. M. Bose for his kind interest in the work. My best thanks are also due to Dr. S. C. Sirkar for helpful suggestions and guidance.

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